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DENTIFRICE CONTAINING PROPELLANT GAS

Description

The invention relates to a propellant gas-containing dental cleaning and care preparation in a dispensing system which on activation of a valve is dispensed as a ribbon of paste or gel and thereafter slowly swells up due to release of the propellant gas and develops a fine-bubbled foam which remains stable for a long time.

Dentifrices are on the market in various forms and serve primarily for cleaning of the surface of the teeth and prevention of tooth and gum diseases. They usually contain a combination of polishing agents, humectants, surfactants, binding agents, flavourings and fluoride-containing as well as antimicrobial active ingredients. Besides dental powders, which owing to their increased abrasiveness play a subordinate role, dentifrices are mainly offered for sale in paste, cream and translucent or transparent gel form. In recent years liquid dental creams and mouthwashes have also increasingly gained in importance. A disadvantage of the products in paste, cream or gel form is their comparatively high viscosity and consequently poor distributability and slow release of the active ingredients and flavourings.

Improved distributability is achieved by foamed dental creams, which are usually dispensed from aerosol dispensers. Such formulations are known from WO 99/22704, WO 82/03975, EP 0 208 009, AU 8542824, DE 22 17 953, DE 36 23 934, JP 5714520 A and JP 5714521 A. The propellant gases used are CFCs, carbon dioxide, oxygen and low-boiling hydrocarbons. Chlorofluorocarbons (CFCs), however, are no longer permitted in many countries because of the ecological harm they cause. Generally, toothpaste foams are emulsions or dispersions which are dispensed from the dispensers in an already foamed form. This has the disadvantage that the amount of active ingredient is often much too low. Such toothpaste foams are usually stable only for a short period. Furthermore, pure hydrocarbon propellant gases are generally not compatible with conventional toothpaste formulations as they are insoluble in them, resulting in phase separation.

The problem therefore was to develop a dental cleaning and care preparation with improved distributability and efficient release of active ingredients and flavour which is initially dispensed from a dispenser as a non-foamed or only slightly foamed gel-like ribbon and which then gradually – particularly when applied in the mouth – forms a mousse-like “tingling” foam with a completely novel sensory feel. A further problem was to optimise the composition such that propellant gas and toothpaste base form a stable dispersion which does not separate or block the conduction system of the dispenser.

This problem was solved according to the present invention by a dentifrice containing

- a) at least one polishing agent
- b) at least one humectant

- c) at least one surfactant
- d) at least one water-insoluble, non-derivatised cellulose

characterised in that together with a propellant gas or mixture of propellant gases it is filled into a dispensing system with a manually activated valve.

The combination of components a)–c) with a water-insoluble, non-derivatised cellulose allows a stable dispersion of the propellant gas/propellant gas mixture to be produced in the compositions according to the invention. Even when stored for prolonged periods the compositions according to the invention are stable against separation of the propellant gas/propellant gas mixture. Blocking of the dispenser conduction system does not occur. Due to the addition of cellulose the compositions according to the invention form particularly stable foams, which do not deliquesce. The proportion of water in the composition according to the invention is 1–60% by wt., preferably 5–50% by wt. and particularly 30–50% by wt. The dentifrice usually has a pH of 5.5–9, preferably 6.5–8.0 and particularly 7.0–7.3.

The compositions according to the invention are suitable for cleaning and care of the teeth and the prevention of tooth and gum diseases. The preparation according to the invention without propellant gas preferably has a viscosity of at least 10000 mPa · s at 25°C (Brookfield RVF rotation viscometer, spindle 3 or 4 at 4 rpm), which firstly enables filling of the composition via the valve head opening of the dispenser and secondly ensures dimensional stability after removal of the preparation from the dispenser, i.e. in particular prevents deliquescence. The preparation can be applied directly, e.g. with a toothbrush, but on dilution with water is also particularly well suited as a mouth rinse as the fine foam is very readily dispersible in water. In order that the compositions according to the invention, together with the propellant gas, can be filled through the valve head opening of the dispenser using conventional filling machines it is advantageous that the viscosity of the preparation without propellant gas is not higher than 100,000 mPa · s at 25°C, a range from 10,000–80,000 mPa · s and in particular between 10,000 and 50,000 mPa · s being preferred (Brookfield RVF rotation viscometer, spindle 3–5, 4 rpm).

A further subject-matter of the invention is a method of dental care and cleaning characterised in that a non-foamed or only slightly foamed ribbon of toothpaste is dispensed from a dispensing system by manual activation of a valve onto an object suitable for mechanical cleaning of the teeth, the said ribbon of toothpaste having an expansion rate of not more than 100% by vol. in 5 seconds at 20°C and normal pressure and then expanding over a interval of 10–100 seconds to not more than six times its volume, and in that the gas-containing toothpaste mousse is used for cleaning the surfaces of the teeth, the interdental spaces and the oral cavity.

1. Propellant gas

Preferably the propellant gas or propellant gas mixture is contained in the compositions according to the invention in an amount of at least 1% by wt. It is also preferred to choose the content of propellant gas not higher than 10% by wt. relative to the total composition, as otherwise the preparation forms too voluminous a foam. It is particularly preferred to use 3–4% by wt. of the propellant gas/propellant gas mixture. The composition according to the invention should be dispensed from the dispenser in the form of a non-foamed or only slightly foamed gel-like ribbon which forms a fine-bubbled mousse on escape of the

propellant gas/propellant gas mixture – preferably inside the mouth. This ensures a higher quantity of active ingredient compared with preparations taken directly from dispensers as a voluminous foam, and improved distributability of the active ingredients compared with conventional dentifrices in cream, gel or paste form, as well as optimising release/development of the flavouring agents. This results, among other things, in a particular intensive, long-lasting feeling of freshness in the mouth. Since part of the propellant gas is preferably not released until the preparation is applied in the mouth, the propellant gases used should be physiologically safe. Preferably the propellant gas contains at least one component which at normal pressure (1 atm) has a boiling point in the range $-5-35^{\circ}\text{C}$, preferably $15-35^{\circ}\text{C}$ and particularly $20-30^{\circ}\text{C}$. Hydrocarbon propellant gases are particularly advantageous owing to their physiological acceptability. In a preferred embodiment the propellant gas contains a C_5 alkane, preferably in an amount of at least 10% by wt. relative to the total quantity of propellant gas. Of these C_5 alkanes – n-pentane, 2-methylbutane (= isopentane) and neopentane – 2-methylbutane with a boiling point of 29°C is preferably suitable. Preferably a mixture of a C_4 alkane and a C_5 alkane is used as propellant gas, with 1 : 3 – 3 : 1 mixtures (weight ratio) of isopentane/isobutane being especially highly suitable according to the invention for ensuring delayed foaming of the dentifrice (post-foaming effect). Such formulations are still gel-like immediately after dispensing from the dispenser and then gradually swell up on the toothbrush to a very stable foam, which forms relatively quickly particularly at body temperature, i.e. on application of the composition inside the mouth. Besides a completely new sensory feel, the delayed release of gas inside the mouth causes in particular improved development of the flavour with an intensified feeling of freshness.

2. Dispenser

The dentifrices, together with the propellant gas or propellant gas mixture liquefied under pressure, are filled into dispensing systems in conventional filling plants. The said dispensing systems are sufficiently pressure-resistant for the propellant gas to be present in the composition in liquefied form. A dispenser suitable for the composition is, for example, a container with a valve made from a rigid material, the said valve being fitted with a device which uses the contraction force of a stretched rubber hose and/or stretched product container for expelling the composition (i.e. dentifrice and propellant gas) stored therein. A dispenser of this type is described for example in EP 69699. The containers supplied by 3D Dispenser-Distributions GmbH under the name FlexPack[®] also use the restoring force of stretched rubber to expel the composition. Preferably suitable in accordance with the invention are containers which contain a folded, essentially gas-impermeable, flexible internal bag made from a chemically inert plastic (e.g. PET) which is surrounded by an elastic, thick-walled rubber hose. Dispensers of this type are described, for example, in US 5,927,551, US 4,964,540 and EP 69738 and are marketed by the firm of Exxel Container under the name Atmos[™] Dispensing System. In combination with such dispensers, even pure butane as propellant gas can produce a post-foaming effect.

Twin-chamber aerosol cans with an internal bag are also preferably suitable as dispensers. They contain the filled material (dentifrice plus liquefied gas) in an internal bag, and in the outer chamber they contain a further propellant gas which serves to expel the composition on activation of the valve. Such systems can be filled either through an opening in the base of the can or – as in the “under cup system” – by lifting the valve.

3. Cellulose

As a consistency regulator, water-insoluble non-derivatised cellulose is an essential component of the composition according to the invention, ensuring the formation of a particularly stable foam. In combination with surfactants and solubility promoters it allows a stable dispersion of the propellant gas in the toothpaste base. In the composition according to the invention it also helps to prevent separation of the liquid and solid components. Cellulose is usually used in an amount of 0.01–5.0% by wt. of active substance, preferably 0.01–2.0% by wt. relative to the total composition.

In the context of the invention water-insoluble is taken to mean solubility of less than 1% by wt. in water at 20°C, i.e. less than 1% by wt. of cellulose is dissolved in 100 g of a saturated aqueous solution at 20°C. In the context of the invention celluloses whose hydroxyl hydrogen atoms are not substituted by other chemical groups are described as non-derivatised.

Cellulose is a ubiquitous skeletal vegetable substance. It can be used in native or purified form. Purified cellulose is preferably suitable for use in oral hygiene, owing to its good physiological acceptability. The molecular weight of cellulose is usually below 800,000, preferably 10,000–700,000 and in particular 20,000–500,000.

Microcrystalline or powdered celluloses supplied for example by J. Rettenmaier & Sons under the name Arbocel[®] or Vitacel[®], are preferably suitable. Cellulose with a mean primary particle size of less than 1 µm, particularly Arbocel[®] CGP 5000, a highly viscous paste of powdered cellulose with thixotropic properties, is particularly preferably suitable. Arbocel[®] celluloses are extremely effective thickening agents which even when used in low concentrations significantly increase the viscosity of compositions, are inert to ionic components and combine well with other thickening agents. Combination with celluloses of the Arbocel[®] type produces formulations which firstly are of sufficiently low viscosity to allow filling via the valve head opening of the dispensing system and secondly, after removal from the dispensing system, develop a stable foam with volume that produces a completely novel sensation in the mouth. The foam developing from the ribbon of gel is stable for several hours.

4. Polishing agents

The polishing agents, cleaning agents or abrasives used are generally water-insoluble inorganic substances which remove the plaque mechanically without damaging the enamel or dentin. The use of very fine-particle polishing agents with a mean particle size of 1–200 µm, preferably 1–50 µm and particularly 1–10 µm can be especially advantageous. The polishing agent is used in the compositions according to the invention in an amount of 5–50% by wt., preferably 8–30% by wt. and particularly 10–20% by wt. relative to the total composition. Frequently it is especially advantageous to use a combination of polishing agents.

The following are suitable in accordance with the invention: silicic acids, water-insoluble metaphosphates such as sodium metaphosphate, calcium phosphates such as tricalcium phosphate, calcium hydrogen phosphate, calcium hydrogen phosphate dihydrate and calcium pyrophosphate, calcium carbonate (chalk), magnesium carbonate, magnesium dihydrogen phosphate, trimagnesium phosphate, aluminium oxide, calcined aluminium

oxide, aluminium hydroxide and aluminium oxide hydrates, hydroxyapatite and various silicates. Sodium hydrogen carbonate may also be used as a polishing agent in accordance with the invention, particularly in combination with other polishing agents.

Preferably the composition contains at least one compound from the group of silicic acids or silicates as polishing agent. Among the silicic acid polishing agents, precipitation and gel silicic acids are preferably suitable as their properties can be widely varied during manufacture and they are particularly highly compatible with fluoride active ingredients. They are also particularly well suited for the production of gel or liquid tooth creams.

Gel silicic acids are produced by reacting sodium silicate solutions with highly aqueous mineral acids to form a hydrosol, ageing to the hydrogel, washing and subsequent drying. If drying is undertaken under gentle conditions to water contents of 15–35% by wt., what are known as hydrogel silicic acids are obtained, as are known for example from US 4,153,680. Drying to water contents below 15% by wt. causes irreversible shrinkage of the previously loose structure of the hydrogel to the dense structure of the xerogel, as it is called. Such xerogel silicic acids are described, for example, in US 3,538,230.

Precipitation silicic acids are produced from aqueous alkali silicate solutions by precipitation with mineral acids under conditions whereby aggregation to the sol and gel cannot occur. Suitable methods for the production of precipitation silicic acids are described, for example, in DE-OS 25 22 486 and DE-OS 31 14 493.

Suitable silicic acid polishing agents according to the invention are commercially available, for example, under the name Sident[®] 8, Zeodent[®] 113 and 623, Sorbosil[®] AC39, Tixosil[®] 123 and 73.

Among the silicates, various aluminium silicates and zirconium silicates are known as polishing agents. Sodium aluminium silicates can also be suitable as polishing agents, e.g. synthetic zeolites, particularly zeolite A.

In addition, particulate organic polymers, e.g. polymethacrylate, polymethacrylate [*sic*] or polyethylene and polypropylene with a mean particle size of approx. 5–15 µm and mean molecular weight of 3000 g/mol can also be used as cleaning agents.

5. Humectants

Humectants are added to tooth creams not only to protect them from drying out but also to provide them with consistency and stability against the cold. Humectants which can be used are toxicologically harmless polyols such as sorbitol, xylitol, glycerol, mannitol, 1,2-propylene glycol or mixtures of these polyols. Polyethylene glycols with molecular weights of 400–2000 may also be included proportionally as constituents in humectants. In a preferred embodiment the preparation according to the invention contains as humectant at least sorbitol, glycerol or xylitol or any mixture of these substances. The humectant or mixture of humectants is present in the overall composition in an amount of 15–85% by wt., preferably 20–70% by wt. and particularly 30–50% by wt. Preferably the composition according to the invention contains a mixture of humectants, particularly with a sorbitol/polyethylene glycol moiety in the weight ratio 10 : (0.1–1).

6. Surfactants

A further improvement in the cleaning action of the dentifrices according to the invention is achieved by the addition of a suitable surfactant or mixture of surfactants. A comprehensive list of suitable surfactants is contained in US 3,988,433, which surfactants are intended to be part of the disclosure of the present application. The addition of surfactants also serves to produce a foam when brushing the teeth, and hence for improved active ingredient distribution, for stabilisation of the propellant gas dispersion and for emulsifying or solubilising the fats, oils, waxes and aroma oils optionally included. The surfactant or surfactant mixture is used in the compositions according to the invention in an amount of 0.1–10% by wt., preferably 0.3–7 and particularly 1–5% by wt. relative to the overall composition. Preferably the composition contains at least one surfactant from the group of anionic surfactants.

Anionic surfactants

Suitable surfactants with a good foaming action are anionic surfactants which also have a certain enzyme-inhibiting action on the bacterial metabolism of plaque. These include alkali and ammonium salts – particularly sodium salts of C₈-C₁₈ alkane carboxylic acids, of alkyl polyglycol ether sulphates with 12–16 C atoms in the linear alkyl group and 2–6 glycol ether groups in the molecule, of linear alkane (C₁₂-C₁₈) sulphonates, sulphosuccinic acid monoalkyl (C₁₂-C₁₈) esters, sulphated fatty acid monoglycerides, sulphated fatty acid alkanol amides, sulphoacetic acid alkyl (C₁₂-C₁₆) esters, acyl sarcosines, acyl taurides and acyl isethionates each with 8–18 C atoms in the acyl group. What is preferred is the use of at least one anionic surfactant, particularly a sodium alkyl sulphate with 12–18 C atoms in the alkyl group. A surfactant of this type is sodium lauryl sulphate, which is commercially available for example under the name Texapon[®] K1296.

Zwitterionic and ampholytic surfactants

Zwitterionic and ampholytic surfactants can also be used, preferably in combination with anionic surfactants. Ampholytic surfactants which can be used in accordance with the present invention include, for example, alkylaminopropane carboxylic acid. The best known and most widespread group of zwitterionic surfactants is that of the betaine surfactants, e.g. alkyl dimethylcarboxymethyl betaine and acylaminoalkyl dimethylcarboxymethyl betaine. Preferably suitable are cocoacylamino propyl dimethyl ammonium glycinate, which are known under the INCI name of cocamidopropyl betaine. Such products are commercially available, for example, under the name Tego-Betain[®] BL 215 and ZF 50 and Genagen[®] CAB.

Non-ionic surfactants

Non-ionic surfactants are particularly suitable for supporting the cleaning action, and among those surfactants the addition products of ethylene oxide on fatty alcohols, fatty acids, fatty acid monoglycerides, sorbitan fatty acid monoesters or methylglucoside fatty acid monoesters are preferred. The added quantity of ethylene oxide should be sufficiently high that the surfactants are water-soluble, i.e. at least 1 g of the product should be clearly soluble in 1 litre of water at 20°C. Non-ionic surfactants that are preferred in accordance with the invention are ethoxylated glyceryl monoalkyl esters with a degree of ethoxylation of 20–60 and a C₈-C₁₈ alkyl chain, for example PEG 30 glyceryl

stearate, which is commercially available e.g. under the name Tagat[®] S and which also acts as a solubility promoter.

However, also suitable as non-ionic surfactants are alkyl (oligo) glycosides with 8–16 C atoms in the alkyl group and a degree of oligomerisation of the glycoside radical of 1–4 alkyl (oligo) glycosides; manufacture and use thereof as surfactants are known, for example, from US A 3,839,318, DE A 20 36 472, EP A 77 167 or WO A 93/10132. With regard to the glycoside radical it is the case that both monoglycosides ($x = 1$) where a monosaccharide group is bound glycosidically to a fatty alcohol with 10 to 16 C atoms, and oligomeric glycosides with a degree of oligomerisation of x to 10 are suitable. The degree of oligomerisation is a statistical mean, the basis of which is a homologue distribution usual for such technical products. Preferably suitable as alkyl (oligo) glycoside is an alkyl (oligo) glycoside of the formula $RO(C_6H_{10}O)_x-H$ wherein R is an alkyl group with 12 to 14 C atoms and x has a mean value from 1 to 4. Amine oxides are also suitable as surfactants.

In order to achieve an intensive cleaning effect in combination with good foaming and adequate solubilisation of the propellant gases, a mixture of anionic and non-ionic surfactants or a mixture of anionic surfactant, non-ionic surfactant and betaine is preferably used in the compositions according to the invention, for example sodium lauryl sulphate/PEG 30 glyceryl stearate/cocamidopropyl betaine.

Solubility promoters

For improved solubilisation of the propellant gases and the oil and wax components optionally contained in the compositions according to the invention there are used, besides ethanol, in particular non-ionic solubility promoters from the group of surfactants. These include in particular, as already mentioned, ethoxylated compounds with a degree of ethoxylation of 20–60. Particularly suitable for this purpose are ethoxylated fatty acid glycerides, ethoxylated fatty acid sorbitan partial esters or fatty acid partial esters of glycerol ethoxylate or sorbitan ethoxylate. Solubility promoters from the group of ethoxylated fatty acid glycerides mainly comprise addition products of 20 to 60 mol ethylene oxide on mono- and diglycerides of linear fatty acids with 12 to 18 C atoms or on triglycerides of hydroxy fatty acids such as oxystearic acid or ricinoleic acid. Further suitable solubility promoters are ethoxylated fatty acid sorbitan partial esters, e.g. addition products of 20 to 60 mol ethylene oxide on sorbitan monoesters and sorbitan diesters of fatty acids with 12 to 18 C atoms. Similarly suitable solubility promoters are fatty acid partial esters of glycerol ethoxylate or sorbitan ethoxylate, i.e. preferably mono- and diesters of C_{12} – C_{18} fatty acids and addition products of 20 to 60 mol ethylene oxide on 1 mol glycerol or on 1 mol sorbitol.

Cationic surfactants

In addition, some cationic surfactants such as alkyltrimethylammonium chloride, alkyl-dimethylbenzylammonium chloride, alkylpyridinium chloride, alkyl-dimethylhydroxyethylammonium chloride, acylimidazolinium methosulphates and acyloxyethyltrimethylammonium chloride are also suitable as surfactants in the preparations according to the invention.

7. Oil/fat and wax components

In a further preferred embodiment the composition according to the invention also contains oil/fat and/or wax components. In combination with the surfactants they enable partial solubilisation of the propellant gas or propellant gas mixture and impart lustre and malleability to the toothpaste base. In accordance with the invention natural, chemically modified and synthetic waxes, fats and oils can be used alone or in any combination. The oil/fat and wax components are included in an amount of 0.1 to 10% by wt., preferably 0.5 to 5% by wt. and particularly 0.8–3% by wt. relative to the overall composition.

Oils/fats

In the context of the invention, by oils and fats are meant di- and triglycerides of liquid to solid consistency and hydrocarbons and silicone oils, which can be of natural or synthetic origin. In accordance with the invention it may be advantageous to use triglycerides and/or a paraffin oil as oil components. These can be of vegetable, animal or synthetic origin.

Di- and triglycerides are the diesters and triesters of fatty acids with glycerol, i.e. acylglycerols in which the glycerol may be esterified with the same or with different fatty acids or fatty acid derivatives (e.g. lecithin). The fatty acids are preferably C₆-C₃₀ fatty acids and these may be saturated or unsaturated and branched or unbranched. These include esterification products of glycerol with naturally occurring fatty acids such as caproic acid, oenanthic acid, caprylic acid, pelargonic acid, capric acid, undecanoic acid, lauric acid, tridecanoic acid, myristic acid, pentadecanoic acid, palmitic acid, margaric acid, stearic acid, nonadecanoic acid, arachidic acid, behenic acid, lignoceric acid, cerotic acid, melissic acid, 2-ethylhexanoic acid, isotridecanoic acid, isostearic acid, palmitoleic acid, oleic acid, elaidic acid, petroselenic acid, elaeostearic acid, erucic acid, linoleic acid, linolenic acid, arachidonic acid, clupanodonic acid, docosahexaenoic acid and gadoleic acid, as well as technical mixtures thereof formed, for example, during the pressure cleaving of natural fats and oils or the dimerisation of unsaturated fatty acids. The use of natural fats and oils such as beef tallow, peanut oil, colza oil, cottonseed oil, soya oil, sunflower oil, palm oil, palm kernel oil, linseed oil, almond oil, castor oil, maize oil, olive oil, rapeseed oil, sesame oil, cocoa butter and coconut oil and the like may be especially suitable. Hydrogenated or hardened oils, e.g. hydrogenated soya oil, castor oil and peanut oil, may also be used.

Also usable in accordance with the invention are low to high-viscosity silicone oils or natural and synthetic hydrocarbons such as low to high-viscosity paraffin oils, isohexadecane, isoeicosan or polydecene, which are available e.g. under the names Emery[®] 3004, 3006, 3010, Ethylflo[®] or Nexbase[®] 20046. The use of what are known as inverse fats (e.g. esters of vicinal tricarboxylic acids with C₆-C₃₀ fatty alcohols) or of glyceryl trialkyl ethers is also conceivable.

Waxes

By waxes are meant substances obtained naturally or synthetically, with the following properties: they are of solid to brittlely hard consistency, coarse to fine-crystalline, transparent to opaque, but not glassy, and melt above 35°C without decomposition. They are low-viscous just above the melting point and not stringy, and exhibit a highly

temperature-dependent consistency and solubility. The most common representatives of the group of waxes are, from a chemical viewpoint, esters of fatty acids and higher fatty alcohols that are of animal and vegetable origin. Usable in accordance with the invention are natural vegetable waxes such as jojoba oil, candelilla wax, carnauba wax, Japan wax, esparto wax, cork wax, guaruma wax, rice germ oil wax, sugarcane wax, ouricury wax, montan wax, sunflower wax, fruit waxes such as orange waxes, lemon waxes, grapefruit wax, bayberry wax, and animal waxes such as beeswax, shellac wax, spermaceti, wool wax and uropygial oil. It may also be advantageous to use hydrogenated or hardened waxes. Natural waxes which may be used according to the invention also include mineral waxes, e.g. ceresin and ozokerite, or the petrochemical waxes such as paraffin waxes (e.g. soft paraffin) and microwaxes. Chemically modified waxes, e.g. montan ester waxes, sasol waxes and hydrogenated jojoba waxes can also be used as the wax component. Synthetic waxes usable according to the invention also include, for example, waxy polyalkylene waxes and silicone waxes.

Also usable in accordance with the invention are synthetic waxes, particularly the esters of C₆-C₃₀ fatty acids with C₆-C₃₀ fatty alcohols, which may be of natural or synthetic origin. Both the fatty acid component and the fatty alcohol component may be straight-chain or branched and saturated or mono- or polyunsaturated.

In accordance with the invention it may be advantageous to select the wax component from the group of vegetable or animal and/or paraffin waxes or from any mixture of these waxes.

8. Further binding agents/thickening agents

In a preferred embodiment the preparation according to the invention additionally contains, besides cellulose, at least one further binding agent or thickening agent which is present in the compositions according to the invention in a total amount of 0.1–5% by wt., preferably 0.1–3% by wt. and particularly 0.5–2% by wt. Examples of substances used are natural and/or synthetic water-soluble polymers such as alginates, carrageens, agar-agar, guar gum, gum arabic, succinoglycan gum, guar flour, carob gum, tragacanth, karaya gum, xanthan, pectins, derivatised cellulose, e.g. carboxymethylcellulose, hydroxyethylcellulose or hydroxypropyl methylcellulose, hydrophobically modified celluloses, starch and starch ethers. Water-soluble carboxyvinyl polymers (e.g. Carbopol[®] grades), polyvinyl alcohol, polyvinylpyrrolidone and higher-molecular polyethylene glycols (particularly those with molecular weights of 10²–10⁶ D) are suitable as further binding and thickening agents. Sheet silicates and fine-particle silicic acids (aerogel silicic acids and pyrogenous silicic acids) can also fulfil this function.

9. Additional active ingredients

A further preferred embodiment of the dentifrice is characterised in that it contains as additional active ingredients anticaries agents, antimicrobial agents, tartar inhibitors, remineralisation agents, flavouring agents or any combination of these substances.

Anticaries agents

Fluorine compounds, preferably from the group of fluorides or monofluorophosphates in an amount of 0.1–0.5% by wt. fluorine, are particularly suitable for controlling and

preventing caries. Suitable fluorine compounds are e.g. sodium fluoride, potassium fluoride, tin fluoride, disodium monofluorophosphate ($\text{Na}_2\text{PO}_3\text{F}$), dipotassium monofluorophosphate or the fluoride of an organic amino compound.

Antimicrobial agents

Phenols, resorcinols, bisphenols, salicyl anilides and amides and halogenated derivatives thereof, halogenated carbonilides and p-hydroxybenzoic acid esters, for example, are suitable as antimicrobial components. Of the antimicrobial components those which inhibit the growth of plaque bacteria are particularly suitable. For example, halogenated diphenylethers such as 2,4-dichloro-2'-hydroxydiphenylether, 4,4'-dichloro-2'-hydroxydiphenylether, 2,4,4'-tribromo-2'-hydroxydiphenylether, 2,4,4'-trichloro-2'-hydroxydiphenylether (Triclosan) are suitable as antimicrobial agents. Besides bromochlorophen, bisbiguanides such as chlorhexidine and alexidine, phenylsalicylic acid esters and 5-amino-1,3-bis(2-ethylhexyl)-hexahydro-5-methylpyrimidine (hexetidine), an antimicrobial action is also exhibited by zinc ions and copper ions, with synergistic effects occurring particularly in combination with hexetidine and Triclosan. Quaternary ammonium compounds, e.g. cetylpyridinium chloride, benzalkonium chloride, domiphen bromide and dequalinium chloride, can also be used. Octapinol, octendine and sanguinarine have also shown themselves to be antimicrobially active. The antimicrobial active ingredients, which can also be added in the form of nano particles, are preferably used in the preparations according to the invention in amounts of 0.01–1% by wt. Particularly preferably, Irgacare[®] MP in an amount of 0.01–0.3% by wt. is used.

Tartar inhibitors

Tartar consists of mineral deposits which are very similar to natural tooth enamel. To inhibit tartar formation substances are added to the dentifrices according to the invention which specifically intervene in crystal nucleus formation and prevent nuclei already present from growing further. Tartar inhibitors are, for example, condensed phosphates, which are preferably selected from the group of tripolyphosphates, pyrophosphates, trimetaphosphates or mixtures thereof. They are used in the form of their alkali or ammonium salts, preferably in the form of their sodium or potassium salts. Aqueous solutions of these phosphates typically exhibit an alkaline reaction, and therefore the pH of the dentifrices according to the invention is adjusted to values of 7.5–9, if required, by the addition of acid. Acids which can be used are e.g. citric acid, phosphoric acid or acid salts, e.g. NaH_2PO_4 . The desired pH of the dentifrice can also be adjusted, however, by the addition of acid salts of condensed phosphates, i.e. $\text{K}_2\text{H}_2\text{P}_2\text{O}_7$ for example.

Mixtures of different condensed phosphates and/or hydrated salts of condensed phosphates may also be used in accordance with the invention. Tartar inhibitors are usually used in the preparations according to the invention in amounts of 0.1–5% by wt., preferably 0.1–3% by wt. and particularly 0.1–2% by wt.

Other suitable tartar inhibitors are organophosphonates such as 1-azacycloheptane-2,2-diphosphonate (sodium salt), 1-hydroxyethane-1,1-diphosphonate (sodium salt) and zinc citrate.

Remineralisation agents

The preparations according to the invention also preferably contain substances which promote remineralisation of enamel and are capable of closing dental lesions. They are usually included in a total amount of 0.1–10% by wt., preferably 0.1–5% by wt. and particularly 0.1–3% by wt. Examples of such substances are fluorides, phosphate salts of calcium, e.g. calcium glycerol phosphates, calcium hydrogen phosphate, hydroxyapatite, fluorapatite, F-doped hydroxyapatite, dicalcium phosphate dihydrate and calcium fluoride. However, magnesium salts such as magnesium sulphate, magnesium fluoride or magnesium monofluorophosphate also have a remineralising effect.

Flavouring agents

The preparations according to the invention preferably contain flavouring agents, which includes e.g. sweetening agents and/or aroma oils. Suitable sweetening agents are, for example, saccharinates (particularly sodium saccharinate), cyclamates (particularly sodium cyclamate) as well as sucrose, lactose, maltose or fructose. Possible aroma oils are all natural and synthetic aromas traditionally used in oral and dental care preparations. Natural aromas may be used both in the form of essential oils isolated from the drugs (mixture) and in the form of the individual components isolated therefrom. The preparations according to the invention should preferably contain at least one aroma oil from the group peppermint oil, spearmint oil, anise oil, star anise oil, caraway oil, eucalyptus oil, fennel oil, cinnamon oil, clove oil, geranium oil, sage oil, pimento oil, thyme oil, origanum oil, basilicon oil, citrus oil, wintergreen oil or one or more components isolated therefrom or one or more synthetically produced components of the said oils. The principal components of the said oils are e.g. menthol, carvone, anethole, cineole, eugenol, cinnamic aldehyde, caryophyllene, geraniol, citronellol, linalool, salvene, thymol, terpinene, terpinol, methyl chavicol and methyl salicylate. Other suitable aromas are e.g. menthyl acetate, vanillin, ionone, linalyl acetate, rhodinol and piperitone.

A particularly preferred embodiment of the dentifrice contains a) 5–30% by wt. of a polishing agent; b) 20–85% by wt. of a humectant; c) 0.3–5% by wt. of a surfactant or surfactant mixture; d) 0.01–5% by wt. of a water-insoluble non-derivatised cellulose; e) 0.05–0.5% by wt. of a fluoride; f) 5–50% by wt. of water; g) 1–10% by wt. of a C₄ and/or C₅-containing propellant gas or propellant gas mixture and [*sic*] in a dispensing system with manually activated valve. This combination allows a particularly good post-foaming effect, high ease of distributability, rapid flavour release and a particularly dimensionally stable foam.

Other usual constituents

The preparation according to the invention can preferably contain a number of other toothpaste constituents. These include:

- vitamins, e.g. retinol, biotin, tocopherol, ascorbic acid and derivatives thereof (e.g. esters, salts);
- pigments, e.g. titanium dioxide or zinc oxide;
- bleaching agents;
- colouring agents;

- pH adjusters and buffers, e.g. sodium citrate, sodium bicarbonate, potassium phosphate or sodium phosphate;
- sodium benzoate;
- wound-healing and anti-inflammatory substances, e.g. allantoin, urea, panthenol, azulene or camomile extract, acetylsalicylic acid derivatives, thiocyanate; hydrogen peroxide;
- zinc sulphate, manganese sulphate.

Examples according to the invention

The dentifrice is manufactured under conditions of degasification, i.e. in a moderate vacuum (≤ 650 mbar), at room temperature.

General instruction

The humectants, silicic acids and, if necessary, further polishing agents were homogenised with desalinated water in a vacuum, with stirring. The soluble salts and colouring agents were then added. The cellulose was suspended in some water and worked in to the mass. Further organic binding agents (e.g. xanthan gum etc.) were dispersed in PEG and then worked in to the mass with stirring. After the mass had swollen, the oil components and surfactants, which had previously been emulsified with each other at 60–85°C, were added, then the flavouring agents, and stirring was continued until a homogenous mass with a smooth structure was obtained.

The paste mass (90–99% by wt.), together with 1–10% by wt. of the propellant gas/propellant gas mixture, was filled into the Atmos™ Dispensing System (70 or 140 ml) of Exxel Container Inc. or into a twin-chamber aerosol can, under the usual conditions for such systems. (filling pressure: approx. 40 bar).

The quantities shown in the examples below relate, unless stated otherwise, to percentage by weight of active substance in the overall composition without propellant gas.

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[*Examples omitted*]

Claims

1. Dentifrice containing
 - a) at least one polishing agent
 - b) at least one humectant
 - c) at least one surfactant
 - d) at least one non-derivatised water-insoluble cellulose**characterised in that**, together with a propellant gas or propellant gas mixture, it is filled into a dispensing system with manually activated valve.
2. Dentifrice according to claim 1, characterised in that the propellant gas contains at least one component with a boiling point of $-5-35^{\circ}\text{C}$.
3. Dentifrice according to any of claims 1 or 2, characterised in that it contains at least 1% by wt. of a propellant gas or propellant gas mixture.
4. Dentifrice according to any of claims 1 to 3, characterised in that the propellant gas contains a C_5 alkane.
5. Dentifrice according to any of claims 1 to 4, characterised in that the propellant gas contains a mixture of a C_4 alkane and a C_5 alkane.
6. Dentifrice according to any of claims 1 to 5, characterised in that it contains at least one polishing agent selected from the group of silicic acids or silicates.
7. Dentifrice according to any of claims 1 to 6, characterised in that it contains at least one humectant selected from the group sorbitol, glycerol, xylitol or any mixture of these substances.
8. Dentifrice according to any of claims 1 to 7, characterised in that it contains at least one surfactant from the group of anionic surfactants.
9. Dentifrice according to any of claims 1 to 8, characterised in that it additionally contains at least one oil and/or wax component.
10. Dentifrice according to any of claims 1 to 9, characterised in that it additionally contains at least one further binding or thickening agent.
11. Dentifrice according to any of claims 1 to 10, characterised in that, as additional active ingredients, it contains anticaries agents, antimicrobial agents, tartar inhibitors, remineralisation agents, flavouring agents or any combination of these substances.
12. Dentifrice according to any of claims 1 to 11, characterised in that the preparation without propellant gas has a viscosity of at least $10,000 \text{ mPa} \cdot \text{s}$ at 25°C .
13. Dentifrice according to any of claims 1 to 12, characterised in that it contains at least
 - a) 5–30% by wt. of a polishing agent
 - b) 20–85% by wt. of a humectant

- c) 0.3–5% by wt. of a surfactant or surfactant mixture
 - d) 0.01–5% by wt. of a water-soluble, non-derivatised cellulose
 - e) 0.05–0.5% by wt. of a fluoride
 - f) 5–50% by wt. water
 - g) 1–10% by wt. of a C₄ and/or C₅-containing propellant gas or propellant gas mixture
- in a dispensing system with manually activated valve.
14. Use of a dentifrice according to any of claims 1 to 13 for cleaning and care of the teeth and for prevention of tooth and gum diseases.
15. Method of dental care and cleaning, characterised in that a non-foamed or only slightly foamed ribbon of toothpaste is dispensed from a dispensing system by manual activation of a valve onto an object suitable for mechanical cleaning of the teeth, the said ribbon of toothpaste having an expansion rate of not more than 100% by vol. in 5 seconds at 20°C and normal pressure and then expanding over an interval of 10–100 seconds to not more than six times its volume, and in that the gas-containing toothpaste mousse is used for cleaning the surfaces of the teeth, the interdental spaces and the oral cavity.